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(54) **Laminated glass with functional ultra-fine particles and method of producing same**

Verbundglasscheibe mit ultrafeinen funktionellen Partikeln und Verfahren zu ihrer Herstellung

Vitrage feuilleté contenant des particules ultrafines fonctionnelles et méthode de fabrication

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Description**BACKGROUND OF THE INVENTION**

[0001] The present invention relates to a laminated glass with an interlayer resinoid film containing functional ultra-fine particles dispersed therein and a method of producing this laminated glass.

[0002] There have been proposed colorless or colored architectural glasses having functions of heat insulation, ultraviolet ray insulation and improved radio wave transmission. Furthermore, there have been proposed automotive glasses having a function of heat insulation for insulating solar radiation energy incident on car interior and thus for lowering the air conditioning load, and a function of ultraviolet ray insulation. Recently, there has been an increasing demand for an architectural or automotive laminated glass having functions of heat insulation, ultraviolet ray insulation, and improved radio wave transmission, while this glass has a sufficient visible light transmittance.

[0003] There are several proposals that fine particles are contained in the interlayer film of laminated glass, for providing the laminated glass with a certain function(s). For example, Japanese Patent Unexamined Publication JP-A-2-22152 discloses an interlayer film of laminated glass, for insulating short wavelength light rays. This interlayer film is made of a plasticized polyvinyl butyral containing at least one light absorbing agent selected from special benzotriazole derivatives and an inorganic matter in the form of fine powder. 90% by weight of this inorganic matter has a particle diameter within a range from 250 to 400 nm. This interlayer film is characterized in that light rays of up to 400 nm wavelength is substantially insulated and that light rays of at least 450 nm wavelength is substantially transmitted therethrough. The light absorbing agent's content is from 0.4 to 6 wt%, and the inorganic matter's content is from 2 to 17 wt%.

[0004] As another example, Japanese Patent Unexamined Publication JP-A-4-160041 discloses an automotive window glass having a layer interposed between transparent platelike members. This layer is made of a mixture of a glass component and ultra-fine particles having an average diameter of up to 0.1 μm. The glass component is an organic silicon or an organic silicon compound and serves to bond together at a relatively low temperature two glass plates of a laminated glass or an interlayer resinoid film and a glass plate. The ultra-fine particles has a function of transparent electric conductiveness, infrared reflection function, electromagnetic insulation function.

[0005] Japanese Patent Unexamined Publication JP-A-4-261842 discloses a laminated glass comprising an organic glass member, a transparent member, and an interlayer film interposed therebetween. This interlayer film contains 100 parts by weight of an ethylene-ethylacrylate copolymerized resin prepared by graft

modification of a vinylsilane and 3-30 parts by weight of optional silicon dioxide fine particles. When the particle diameter of the fine particles is from 0.1 to 400 nm, scatter of light rays which are transmitted through the interlayer film can be prevented.

SUMMARY OF THE INVENTION

[0006] It is an object of the present invention to provide a laminated glass which has a good quality requisite for an architectural or automotive laminated glass itself and of which interlayer film has various additional functions such as heat insulation, ultraviolet ray absorption and the maintenance of a sufficient radio transmittance.

[0007] According to a first aspect of the present invention, there is provided a laminated glass as defined in claim 1.

[0008] According to a second aspect of the present invention, there is provided a method of producing a laminated glass as defined in claim 10.

[0009] As is mentioned above, a laminated glass according to the present invention has an interlayer film containing ultra-fine particles which have a particle diameter of up to 0.2 μm and are dispersed in the interlayer film. With this, the laminated glass has various additional functions such as the provision of colorlessness or a certain desired color tone, heat insulation, ultraviolet ray insulation, the maintenance of a sufficient radio transmittance, and the like, without adding an adverse effect on the interlayer film's basic characteristics requisite for an architectural or automotive laminated glass. Therefore, the laminated glass is capable of improving the air conditioning effect and inhabitability of automobile, building and the like, of reducing an adverse effect of ultraviolet rays on the interior of automobile, building or the like, and of maintaining a sufficient radio transmittance equivalent to that of a conventional float glass, for receiving and transmitting radio waves.

[0010] A laminated glass according to the present invention is well controlled in color tone, extremely low in haze value, and superior in transparency and in reduction of reflection and glare. For example, the laminated glass has requisite basic characteristics for an automotive safety glass. These basic characteristics are substantially equivalent to those of conventional automotive laminated glass and provide satisfactory results in various tests of Japanese Industrial Standard (JIS) R 3212 and the like.

[0011] In a method of producing a laminated glass according to the present invention, it is not necessary to use a glass plate having a special composition nor a glass plate having a special surface finish. A conventional production line for producing conventional laminated glasses can be used for producing a laminated glass of the present invention. Therefore, the laminated glass can be easily and economically produced. Furthermore, it can be flexibly produced according to the

size and shape of the laminated glass.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0012] In the following, a laminated glass according to the present invention as defined in claims 1 and 10 will be described in detail. This laminated glass comprises first and second transparent glass plates and an interlayer film interposed therebetween. The interlayer film has functional ultra-fine particles which have a particle diameter of up to 0.2 µm and are dispersed therein. These particles are used to provide various functions such as heat insulation, thereby maintaining the solar radiation transmittance within a range of up to 65%, while the scattering and reflection of the visible light rays is suppressed. In spite of the fact that the interlayer film contains the functional ultra-fine particles, it has been unexpectedly found that the laminated glass has an extremely low haze value, a good radio transmittance and a sufficient transparency and that the interlayer film is sufficient in bond strength against the first and second glass plates, in transparency, durability and the like. Even though the interlayer film contains the functional ultra-fine particles, the laminated glass can be produced in a production line for conventional laminated glasses. The functional ultra-fine particles have a particle diameter preferably up to 0.15 µm or from 0.001 to 0.2 µm, more preferably from 0.001 to 0.15 µm or from 0.002 to 0.15 µm, and still more preferably from about 0.001 to about 0.10 µm or from about 0.002 to about 0.10 µm. It is preferable that these particles have a narrow particle diameter distribution, for example, within a range about 0.01 to about 0.03 µm.

[0013] In the invention the functional ultra-fine particles amount to up to 10.0 wt% based on the total weight of the interlayer film. With this, these particles have various functions such as heat insulation, for example, to maintain the solar radiation transmittance within a range of up to 65%, while a first condition that the laminated glass has an extremely low haze value, a sufficient radio transmittance and a sufficient transparency is satisfied, while a second condition that the interlayer film is sufficient in bond strength against the first and second glass plates, in transparency, durability and the like is satisfied, and while a third condition that the laminated glass can be produced by a production line for conventional laminated glasses is satisfied. If the amount of the functional ultra-fine particles exceeds 10.0 wt%, it becomes difficult to satisfy the above-mentioned first, second and third conditions. When the laminated glass is used as an architectural glass having a visible light transmittance (Tv) of at least 35%, it is necessary to add the ultra-fine particles made of inorganic pigment(s) in an amount within a range from about 0.1 to about 10 wt%. In general, in the production of the laminated glass as an architectural glass, the amount of the ultra-fine particles is preferably from about 0.01 to about 9 wt% and

more preferably from about 0.05 to about 8 wt%. In general, in the production of the laminated glass as an automotive glass, the amount of these particles is preferably from about 0.01 to about 2.0 wt% and more preferably from about 0.1 to about 1.0 wt%. In conclusion, the amount of these particles is decided according to the balance between the above-mentioned additional functions of these particles and the basic characteristics of the laminated glass. That is, if the amount of these particles is too much, the additional functions of these particles become sufficient, but the basic characteristics of the laminated glass may be impaired. On the contrary, if the amount of these particles is too little, the basic characteristics of the laminated glass are maintained, but the additional functions of these particles become insufficient.

[0014] In the invention, the interlayer film is made of a polyvinyl butyral (PVB) or an ethylene-vinylacetate copolymer (EVA), which is generally used as a material for the interlayer film. Examples of the material of the interlayer film are a plasticized PVB made by Sekisui Chemical Industries, Ltd., Monsant Japan, Ltd. or the like, an EVA made by Du pont Co. or Takeda Chemical Industries, Ltd. (DUMILAN (trade name)), and a modified EVA

(e.g., MERUCENE G (trade name) made by Toso Co.). It is optional to add an additive(s) to the interlayer film, such as ultraviolet absorbing agent, antioxidant, anti-static agent, heat stabilization agent, lubricant, filler, coloring agent, and bond adjusting agent.

[0015] It is optional that the interlayer film according to the present invention is placed on a conventional interlayer film to prepare a laminate, and then this laminate is interposed between the first and second glass plates to prepare the laminated glass. Furthermore, it is optional that the interlayer film according to the present invention is interposed between first and second conventional interlayer films to prepare a laminate to be interposed between the first and second glass plates.

[0016] In the invention the ultra-fine particles comprise at least one member selected from the group consisting of

- (1) ATO which is defined as being an antimony-doped tin oxide, SnO₂ doped with Sb, SnO₂ doped with Sb₂O₃, a conductive antimony-containing tin oxide or a solid solution of tin oxide and antimony oxide,
- (2) ITO which is defined as being a tin-doped indium oxide, a mixture of In₂O₃ and SnO₂, an indium tin oxide, a conductive tin-containing indium oxide, In₂O₃ doped with Sn or a solid solution of indium oxide and tin oxide,
- (3) a mixture of Co₂O₃ and Al₂O₃,
- (4) a mixture of TiO₂, NiO, Co₂O₃ and ZnO, and
- (5) a mixture of Fe₂O₃, ZnO and Cr₂O₃.

The functional ultra-fine particles may comprise a mixture of the above-mentioned at least one member and

an organic resin. This mixture may be the at least one member coated with this organic resin.

[0017] Examples of the metals doped with the at least one substance are SnO₂ doped with 9 wt% Sb₂O₃ (ATO) made by Sumitomo Osaka Cement Co., SnO₂ doped with fluorine, and SnO₂ doped with 10 wt% Sb₂O₃. Examples of mixtures (composites) each containing at least two of the above-mentioned metals are In₂O₃-5wt% SnO₂ (ITO) made by Mitsubishi Material Co., and inorganic pigment ultra-fine particles such as Co₂O₃-Al₂O₃ (e.g., TM3410 (trade name) having a particle diameter from 0.01 to 0.02 μm), TiO₂-NiO-Co₂O₃-ZnO (e.g., TM3320 (trade name) having a particle diameter from 0.01 to 0.02 μm) and Fe₂O₃-ZnO-Cr₂O₃ (e.g., TM3210 (trade name) having a particle diameter from 0.01 to 0.02 μm). TM3410, TM3320 and TM3210 are made by Dai Nichi Seika Kogyo Co. Examples of the above-mentioned organic resin to be used together with the above-mentioned at least one member are fluorine compounds such as fluororesins, polytetrafluoroethylene (PTFE), LUBURON (trade name) made by Daikin Industries, Ltd., CEFRAL LUBE (trade name) of Central Glass Co., Ltd., and low molecular weight trifluoroethylene (TFE), silicone resins, silicone rubbers. Of the above examples, ATO and ITO are particularly preferable examples as the functional ultra-fine particles for an automotive laminated glass.

[0018] The above-mentioned organic resin is used to reduce bond strength between the PVB film and the first and second glass plates. In other words, in case that, for example, ATO or ITO is used as the functional ultra-fine particles, the bond strength may become too much. In this case, the organic resin is used to lower the pull-out value and thus to reduce the bond strength to a permissible standard range. Thus, the purpose of the addition of the organic resin is similar to that of the primer coating on the glass plate surface or to that of the coating of the organic resin film made of fluororesin, silicone resin, silicone rubber or the like.

[0019] By the incorporation of the functional ultra-fine particles into the interlayer film, the laminated glass is provided with various functions such as heat insulation, ultraviolet ray insulation, the provision of colorlessness or a certain desired color tone, light insulation and the like.

[0020] In the Invention, the interlayer may contain an organic ultraviolet-ray-absorbing agent. Examples of this agent are benzotriazole derivatives such as 2-(2'-hydroxy-5'-methylphenyl) benzotriazole, 2-(2'-hydroxy-3',5'-ditert-butylphenyl) benzotriazole, 2-(2'-hydroxy-3'-tert-butyl-5'-methylphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-3',5'-ditert-butylphenyl)-5-chlorobenzotriazole and 2-(2'-hydroxy-3',5'-ditert-amylphenyl) benzotriazole, benzophenone derivatives such as 2,4-dihydroxybenzophenone, 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-octoxybenzophenone, 2-hydroxy-4-dodecyloxybenzophenone, 2,2'-dihydroxy-4-methoxybenzophenone, 2,2'-dihydroxy-4,4'-dimethoxybenz-

ophenone and 2-hydroxy-4-methoxy-5-sulfobenzophenone, and cyanoacrylate derivatives such as 2-ethylhexyl-2-cyano-3,3'-diphenylacrylate and ethyl-2-cyano-3,3'-diphenylacrylate. An example of commercial products of the organic ultraviolet-ray-absorbing agent is TINUVIN327 (trade name) made by Ciba-Gely Co.

[0021] In the invention, the interlayer film may contain an organic heat-absorbing agent(s). Examples of this agent are NIR-AM1 made by Teikoku Chemical Industries, Ltd., and as near infrared rays absorbing agents SIR-114, SIR-128, SIR-130, SIR-132, SIR-169, SIR-103, PA-1001 and PA-1005 which are made by Mitsui Toatsu Chemicals, Inc. The interlayer film may further contain a pigment(s).

[0022] A laminated glass according to the present invention can be used as an architectural window glass or an automotive window glass such as a front windshield, a rear windshield with or without a shade band, a side windshield, or a sunroof.

[0023] In general, the sheet (surface) resistivity of a glass plate with glass antenna is preferably at least 20 kΩ/□. In particular, when the glass plate is in contact with the antenna, the sheet resistivity is preferably at least 10 MΩ/□. If it is less than 10 MΩ/□, the difference between the sheet resistivity of a laminated glass and that of a glass plate itself may be at least 1 dB as an absolute value. The sheet resistivity of the laminated glass is preferably at least 15 MΩ/□ for maintaining this difference within 0.8 dB (absolute value). The sheet resistivity of the laminated glass is preferably within a range from about 20 MΩ/□ to about 10 GΩ/□ and more preferably within a range from about 22 MΩ/□ to about 10 GΩ/□ for obtaining a satisfactory radio wave transmittance, satisfactory optical characteristics and satisfactory physical and chemical characteristics.

[0024] In the invention, it is possible to obtain a laminated glass which is superior in radio wave transmittance, heat insulation, ultraviolet rays insulation and optical characteristics. This laminated glass is particularly suitable as an automotive windshield. In more detail, this laminated glass as an automotive windshield has a radio transmittance which is equivalent to that of a glass plate itself, a solar radiation transmittance of up to 65% thereby improving a so-called automotive inhabitability, a visible light transmittance of at least 65% or at least 70% thereby allowing the driver and a passenger(s) to have a good view, and a very low visible light reflectance thereby allowing the driver and a passenger(s) to have a good view, avoid misreading of traffic control signal and the like, and minimize the eye fatigue. As an automotive glass plate, it is preferable that the laminated glass has a visible light transmittance of at least 68 or 70%, a visible light reflectance of up to 14%, a solar radiation transmittance of up to 60%, and an excitation purity of up to 15 or 10%. As an architectural glass plate, it is preferable that the laminated glass has a visible light transmittance of at least 30%, a visible light reflectance of up to 20%, a solar radiation transmittance of up to

65%, and an excitation purity of up to 20%.

[0025] The arrangement of the interlayer film is flexible according to need. In other words, for example, the interlayer film may be sized and arranged such that the interlayer film is not formed on a position corresponding to the peripheral portion of the laminated glass, nor on a position corresponding to the feeding point(s), nor on a position corresponding to a portion on which a molding is formed, nor on a position corresponding to the whole or a part of the electric conductor portion of an antenna.

[0026] According to the invention, the interlayer film has a heat insulation characteristic and a high sheet-resistivity equivalent to that of a semiconductor film or of an insulating film. Therefore, the laminated glass of the invention does not cause radio disturbance in receiving AM radio waves, FM radio waves and the like, nor radio interference such as ghost image of the TV picture. Even in case that a film which has a high resistivity and a heat insulation characteristic is formed on a glass antenna device, the radio receiving capacity of the laminated glass is not lowered.

[0027] The first and second glass plates of the laminated glass may be made of an organic glass or a composite glass of inorganic and organic materials and may be colorless or colored float glass plates. This colored float glass plates may have a color of green, bronze, gray or blue. The first and second glass plates may be flat or curved and used for a multiple glass, a by-layer glass, or the like. In general, it is preferable that the first and second glass plates have a thickness, for example, from about 1.0 mm to about 12 mm. For architectural use, these plates have a thickness preferably from about 2.0 mm to about 10 mm. For automotive use, these plates have a thickness preferably from about 1.5 mm to about 3.0 mm and more preferably from about 2.0 mm to about 2.5 mm.

[0028] In the following, a method of producing a laminated glass will be described in detail in accordance with the present invention as defined in claim 10. This method comprises the steps of:

- (a) Interposing an interlayer film between first and second glass plates, the interlayer film having functional ultra-fine particles which are dispersed therein and have a particle diameter of up to 0.2 µm; and
- (b) bonding together the first and second glass plates and the interlayer film.

[0029] It is preferable that the step (b) is conducted in an autoclave by a common autoclave method, or under reduced pressure for a period of time from 20 to 30 minutes, while an ambient temperature was raised from 80 to 120 °C. With this, the interlayer film will have uniformly uneven embossing thereon. However, in some cases, the step (b) may be conducted by one of various simpler methods.

[0030] In the following, a method of preparing the interlayer film will be described in detail in accordance with

the present invention. This method comprises the steps of:

- 5 (c) dispersing up to 80.0 wt% of the functional ultra-fine particles in a plasticizer solution, based on the total weight of the plasticizer solution and the ultra-fine particles, so as to prepare a first mixture;
- 10 (d) adding up to 50 wt% of the first mixture to a PVB or to an EVA, based on the total weight of the PVB or EVA, so as to prepare a second mixture;
- 15 (e) optionally adding at least one additive to the second mixture so as to prepare a third mixture; and
- (f) kneading the third mixture to uniformly disperse therein the functional ultra-fine particles, thereby to prepare a raw material of the interlayer film.

[0031] During the step (c), the functional ultra-fine particles can be well uniformly dispersed in the plasticizer solution. Therefore, the first mixture becomes superior in transparency. During the step (c), if the amount of the functional ultra-fine particles exceeds 80.0 wt%, it becomes difficult to get uniformly dispersed ultra-fine particles. The amount of the ultra-fine particles is preferably up to about 20.0 wt%, more preferably up to about 10.0 wt%, and still more preferably within a range from 0.5 to 5.0 wt%. If the amount of the ultra-fine particles is too small, the advantageous effect of the addition may become insufficient.

[0032] During the step (d), if the amount of the first mixture exceeds 50 wt%, the ultra-fine particles may not be uniformly dispersed in the PVB or the EVA, and the interlayer film's basic characteristics may become unsatisfactory. During the step (d), the amount of the first mixture is preferably up to about 45 wt% and more preferably within a range from about 10 wt% to about 40 wt%. During the step (f), the third mixture is kneaded by a common mixer, Banbury mixer, Brabender plastograph, a kneader, or the like.

[0033] Examples of the plasticizer are phthalic acid esters such as dioctyl phthalate (DOP), diisodecyl phthalate (DIDP), dodecyl phthalate and butylbenzyl phthalate (BBP), phosphoric acid esters such as tricresyl phosphate (TCP) and triethyl phosphate (TOP), fatty acid esters such as tributyl citrate and methylacetyl ricinolate (MAR), polyether esters such as triethyleneglycol-di-2-ethylbutylate (3GH) and tetraethyleneglycoldihexanol, and mixtures of these compounds.

[0034] Examples of solvents for dissolving therein a PVB are ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol and methylene chloride. Examples of solvents for dissolving therein an EVA are toluene, xylene and methylene chloride.

[0035] After the step (f), the raw material is shaped into the interlayer film using a common extruder, a calender or the like. The thickness of the interlayer film is preferably from about 0.2 to about 1.2 mm and more preferably from about 0.3 to about 0.9 mm.

[0036] There is provided an alternative method of pre-

paring the interlayer film according to the present invention. This alternative method comprises the steps of:

- (c) uniformly dispersing the functional ultra-fine particles having a particle diameter within a range from 0.001 to 0.2 μm , in a solvent which is capable of dissolving therein a PVB or an EVA, so that a first mixture is prepared;
- (d) adding the PVB or the EVA, an optional plasticizer and at least one other optional additive to the first mixture, so that a second mixture in which the PVB or the EVA is dissolved is prepared;
- (e) kneading the second mixture;
- (f) shaping the kneaded second mixture into a wet film; and
- (g) drying the wet film at a temperature from 50 to 110 °C into the interlayer film.

[0037] There is provided a further alternative method of preparing the interlayer film in accordance with the present invention. This further alternative method comprises the steps of:

- (c) heating a PVB or an EVA at a temperature which is higher than a glass transition temperature thereof, the glass transition temperature being within a range from 55 to 90 °C, so that the PVB or the EVA is softened; and
- (d) adding functional ultra-fine particles having a particle diameter from 0.001 to 0.2 μm to the softened PVB or EVA, so that a first mixture is prepared; and
- (e) kneading the first mixture so as to uniformly disperse therein the functional ultra-fine particles, thereby preparing the raw material of the interlayer film.

[0038] The following examples are illustrative of the present invention, but these examples are not limitative.

EXAMPLE 1

[0039] In this example, an interlayer film was prepared as follows. At first, 10 g of a dioctyl phthalate solution containing 20 wt% of ATO (conductive antimony-containing tin oxide) ultra-fine particles which have a particle diameter up to 0.02 μm and are dispersed therein, and 130 g of pure dioctyl phthalate were added to 485 g of a polyvinyl butyral resin. Then, this mixture was kneaded at about 70 °C for about 15 min, with the addition of an ultraviolet ray absorbing agent and the like, by a mixer equipped with three rollers. The thus obtained raw material of the interlayer film was shaped at about 190 °C by an extruder into a film having a thickness of about 0.8 mm. With this, uniformly uneven embossing was formed on the surface of the interlayer film.

[0040] The thus prepared interlayer film was cut to have the same size as that of two clear glass substrates

(FL2.3) having widths of about 300 mm and a thickness of about 2.3 mm. Then, the interlayer film was interposed between these glass substrates to prepare a laminate. Then, this laminate was put into a vacuum bag made of rubber. Then, the atmosphere of this bag was removed to reduce pressure thereof, and under this condition this bag was allowed to stand still for about 20-30 minutes at a temperature from about 80 to 110 °C. Then, the temperature was lowered to room temperature.

- 5 Then, the laminate was taken out of the bag and then put into an autoclave. Then, the laminate was heated at a temperature from about 110 to about 140 °C under a pressure from about 0.98 to about 1.37 MPa (about 10 to about 14 kg/cm²) for a period of time from about 20 to 15 to about 40 minutes for bonding together the glass substrates and the interlayer film.

[0041] The thus obtained laminated glass was subjected to several evaluation tests, as follows. In optical characteristics tests, the transmittance of the laminated glass for the light having a wavelength from 340 to 1,800 nm was measured with 340 type automated spectrophotometer (trade name) made by Hitachi Ltd. With this, the visible light transmittance T_v (380-780 nm), the solar radiation transmittance T_s (340-1,800 nm), excitation purity (P_e) and the color tone of the laminated glass were determined in accordance with Japanese Industrial Standard (JIS) Z 8722 and JIS R 3106 OR JIS Z 8701. In these tests, T_v was about 76.8 %, T_s was about 58.6 %, P_e was about 0.7%, and the color tone was a neutral pale gray. The laminated glass did not have glare caused by reflection.

[0042] The haze value (H) was determined in accordance with JIS K6714. Haze values of up to 3% and up to 1% were judged as being satisfactory as architectural and automotive laminated glasses, respectively. The result of this haze value test was about 0.3%.

[0043] In radio wave transmittance test, the value of reflection loss (dB) of the laminated glass within a radio wave frequency from 10 to 1,000 MHz was compared with that of a clear glass plate (FL3t) in accordance with the KEC method using an electric field shield effect meter. The laminated glass was judged as being satisfactory in this test, because the result of the laminated glass according to this example was equivalent to that of the clear glass plate, and because the absolute value of the difference therebetween was not greater than 2 dB.

[0044] In bond strength test, the laminated glass was allowed to stand still at a temperature from -18.6 to -17.4 °C for a period of time from 12 to 20 hr. Then, the laminated glass was hit by a hammer to break the glass plate thereof. The laminated glass was judged as being satisfactory, because the degree of exposure of the interlayer film was not significant.

[0045] In a heat resistance test, the laminated glass was put into boiling water at 100 °C for about 2 hr. The laminated glass was judged as being satisfactory, because the laminated glass, except its peripheral portion having a width of 10 mm, after this test did not have ab-

normalities such as the occurrence of bubbles, clouds, cracks and the like.

[0046] In a humidity resistance test, the laminated glass was allowed to stand still in an atmosphere of a temperature from 48 to 52 °C and a humidity from 91 to 99% for two weeks. The laminated glass was judged as being satisfactory, because the laminated glass after this test did not have abnormalities such as the occurrence of bubbles, clouds, crack and the like.

[0047] In an electrical characteristic test, the sheet resistivity of the laminated glass was measured with a surface resistivity meter (HIRESTA HT-210 (trade name) made by Mitsubishi Petrochemical Co., Ltd.). In this test, the laminated glass was judged as being satisfactory because it had a sheet resistivity of at least 10 MΩ/□.

[0048] In addition to the above-mentioned tests, a weatherability test and some other tests were conducted. The laminated glass was judged as being satisfactory in these tests, too. For example, the visible light transmittance was determined before and after the weatherability test for about 1,000 hr with a sunshine weathermeter. The laminated glass had substantially the same transmittance before and after this test. Therefore, it was judged as being satisfactory in this test.

EXAMPLE 2

[0049] In this example, an interlayer film was prepared as follows. At first, 10 g of a triethyleneglycol-di-2-ethylbutyrate (3GH) solution containing 20 wt% of ATO (conductive antimony-containing tin oxide) ultra-fine particles which have a particle diameter up to 0.02 μm and are dispersed therein, and 130 g of pure 3GH were added to 485 g of a polyvinyl butyral resin. Then, this mixture was kneaded at about 70 °C for about 15 min, with the addition of 5 g of a bond adjusting agent (TOSPEARL120 (trade name) made by Toshiba Silicone Co.), an ultraviolet ray absorbing agent and the like, by a mixer equipped with three rollers. The thus obtained raw material of the interlayer film was shaped at about 190 °C by an extruder into a film having a thickness of about 0.8 mm. With this, uniformly uneven embossing was formed on the surface of the interlayer film.

[0050] The thus prepared interlayer film was cut to have the same size as that of two clear glass substrates (FL2) having widths of about 300 mm and a thickness of about 2.0 mm. Then, the interlayer film was interposed between these glass substrates to prepare a laminate. Then, a laminated glass was prepared from this laminate in the same manner as in Example 1.

[0051] The same evaluation tests as those of Example 1 were conducted on the laminated glass. The laminated glass was satisfactory with respect to each evaluation test. For example, T_v was 76.5%, T_s was 58.5%, and H was 0.4%.

EXAMPLE 3

[0052] In this example, an interlayer film was prepared as follows. At first, 10 g of a butylbenzyl phthalate (BBP) solution containing 20 wt% of ITO (conductive tin-containing Indium oxide) ultra-fine particles which have a particle diameter up to 0.1 μm and are dispersed therein, and 90 g of pure BBP were added to 323 g of a polyvinyl butyral resin. Then, from this mixture, an interlayer film having a thickness of about 0.8 mm was prepared

in the same manner as in Example 1. With this, uniformly uneven embossing was formed on the surface of the interlayer film.

[0053] Using the thus prepared interlayer film and the same two glass substrates as those of Example 2, a laminated glass was prepared in the same manner as in Example 1.

[0054] The same evaluation tests as those of Example 1 were conducted on the laminated glass. The laminated glass was satisfactory with respect to each evaluation test. For example, T_v was 76.3%, T_s was 51.5%, and H was 0.4%. Furthermore, the pummel value was about 7-8. Therefore, the laminated glass was judged as being suitable as an architectural laminated glass.

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EXAMPLE 4

[0055] In this example, Example 3 was repeated except in that 5 g of a bond adjusting agent (TOSPAL120 (trade name) made by Toshiba Silicone Co.) was additionally added in the preparation of the raw material of the interlayer film. Then, an interlayer film having a thickness of about 0.8 mm was prepared in the same manner as in Example 1. With this, uniformly uneven embossing was formed on the surface of the interlayer film.

[0056] Using the thus prepared interlayer film and the same two glass substrates as those of Example 2, a laminated glass was prepared in the same manner as in Example 1.

[0057] The same evaluation tests as those of Example 1 were conducted on the laminated glass. The laminated glass was satisfactory with respect to each evaluation test. For example, T_v was 76.2%, T_s was 51.6%, and H was 0.4%. Furthermore, the pummel value was about 3-4. Therefore, the laminated glass was judged as being suitable as an automotive laminated glass.

EXAMPLE 5

[0058] In this example, Example 3 was repeated except in that 10 g of an organic heat-absorbing agent was additionally added in the preparation of the raw material of the interlayer film. Then, an interlayer film having a thickness of about 0.8 mm was prepared in the same

manner as in Example 1. With this, uniformly uneven embossing was formed on the surface of the interlayer film.

[0059] Using the thus prepared interlayer film and the

same two glass substrates as those of Example 2, a laminated glass was prepared in the same manner as in Example 1.

[0060] The same evaluation tests as those of Example 1 were conducted on the laminated glass. The laminated glass was satisfactory with respect to each evaluation test. For example, T_v was 64.3%, T_s was 32.8%, and H was 0.4%.

EXAMPLE 6

[0061] In this example, an interlayer film was prepared as follows. At first, 7 g of a dilsoodecyl phthalate (DIDP) solution containing 20 wt% of ITO (conductive tin-containing indium oxide) ultra-fine particles which have a particle diameter up to 0.1 μm and are dispersed therein, and 95 g of pure DIDP were added to 323 g of a polyvinyl butyral resin. Then, from this mixture, an interlayer film having a thickness of about 0.8 mm was prepared in the same manner as in Example 1. With this, uniformly uneven embossing was formed on the surface of the interlayer film.

[0062] Using the thus prepared interlayer film, one glass substrate which is the same as one of those of Example 1, and another green glass substrate (NFL2), a laminated glass was prepared in the same manner as in Example 1.

[0063] The same evaluation tests as those of Example 1 were conducted on the laminated glass. The laminated glass was satisfactory with respect to each evaluation test. For example, T_v was 73.3%, T_s was 42.0%, and H was 0.2%.

EXAMPLE 7

[0064] In this example, Example 6 was repeated except in that 5 g of a bond adjusting agent (TOSPEARL120 (trade name) made by Toshiba Silicone Co.) was additionally added in the preparation of the raw material of the interlayer film. Then, an interlayer film having a thickness of about 0.8 mm was prepared in the same manner as in Example 1. With this, uniformly uneven embossing was formed on the surface of the interlayer film.

[0065] Using the thus prepared interlayer film and the same two glass substrates as those of Example 6, a laminated glass was prepared in the same manner as in Example 1.

[0066] The same evaluation tests as those of Example 1 were conducted on the laminated glass. The laminated glass was satisfactory with respect to each evaluation test. For example, T_v was 73.2%, T_s was 42.1%, and H was 0.2%.

EXAMPLE 8

[0067] In this example, Example 6 was repeated except in that the green glass substrate was replaced by

a blue glass substrate (BFL2) in the preparation of the laminated glass.

[0068] The same evaluation tests as those of Example 1 were conducted on the laminated glass. The laminated glass was satisfactory with respect to each evaluation test. For example, T_v was 76.0%, T_s was 49.5%, and H was 0.2%.

EXAMPLE 9

[0069] In this example, Example 6 was repeated except in that the green glass substrate was replaced by a bronze glass substrate (MFL2) in the preparation of the laminated glass.

[0070] The same evaluation tests as those of Example 1 were conducted on the laminated glass. The laminated glass was satisfactory with respect to each evaluation test. For example, T_v was 75.1%, T_s was 52.1%, and H was 0.2%.

EXAMPLE 10

[0071] In this example, Example 6 was repeated except in that the green glass substrate was replaced by a gray glass substrate (GFL2) in the preparation of the laminated glass.

[0072] The same evaluation tests as those of Example 1 were conducted on the laminated glass. The laminated glass was satisfactory with respect to each evaluation test. For example, T_v was 76.0%, T_s was 54.5%, and H was 0.2%.

EXAMPLE 11

[0073] In this example, an interlayer film was prepared as follows. At first, 20 g of a DOP solution and 120 g of pure tricresyl phosphate (TCP) were added to 480 g of a polyvinyl butyral resin to prepare a mixture. This DOP solution contained 40 wt% of TM3410 (trade name) made by Dainichi Seika Kogyo Co., that is, ultra-fine particles of an inorganic pigment mixture of Co_2O_3 and Al_2O_3 , which have a particle diameter from 0.01 to 0.02 μm and are dispersed in the solution. Then, an interlayer film having a thickness of about 0.8 mm was prepared from the above mixture in the same manner as in Example 1. Using the thus prepared interlayer film, a laminated glass was prepared in the same manner as in Example 1.

[0074] The same evaluation tests as those of Example 1 were conducted on the laminated glass. The laminated glass was satisfactory with respect to each evaluation test. For example, T_v was 73.8%, T_s was 50.2%, P_e was 7.8%, and H was 0.2%. The laminated glass had a clear blue color tone.

EXAMPLE 12

[0075] In this example, an interlayer film was pre-

pared as follows. At first, 30 g of a DOP solution and 100 g of pure methylacetyl ricinolate (MAR) were added to 480 g of a polyvinyl butyral resin to prepare a mixture. This DOP solution contained 30 wt% of TM3320 (trade name) made by Dainichi Seika Kogyo Co., that is, ultra-fine particles of an inorganic pigment mixture of TiO_2 , NiO , Co_2O_3 and ZnO which have a particle diameter from 0.01 to 0.02 μm and are dispersed in the solution. Then, an interlayer film having a thickness of about 0.8 mm was prepared from the above mixture in the same manner as in Example 1. Using the thus prepared interlayer film, a laminated glass was prepared in the same manner as in Example 1.

[0076] The same evaluation tests as those of Example 1 were conducted on the laminated glass. The laminated glass was satisfactory with respect to each evaluation test. For example, T_v was 77.8%, T_s was 60.2%, and H was 0.2%. P_e was 13.8%, and thus the laminated glass had a clear green color tone.

EXAMPLE 13

[0077] In this example, an interlayer film was prepared as follows. At first, 20 g of a DOP solution and 150 g of pure 3GH were added to 480 g of a polyvinyl butyral resin to prepare a mixture. This DOP solution contained 30 wt% of TM3210 (trade name) made by Dainichi Seika Kogyo Co., that is, ultra-fine particles of an inorganic pigment mixture of Fe_2O_3 , ZnO and Cr_2O_3 which have a particle diameter from 0.01 to 0.02 μm and are dispersed in the solution. Then, an interlayer film having a thickness of about 0.8 mm was prepared from the above mixture in the same manner as in Example 1. Using the thus prepared interlayer film, a laminated glass was prepared in the same manner as in Example 1.

[0078] The same evaluation tests as those of Example 1 were conducted on the laminated glass. The laminated glass was satisfactory with respect to each evaluation test. For example, T_v was 67.8%, T_s was 51.8%, and H was 0.2%. P_e was a slightly high value, but the laminated glass had a clear green color tone.

EXAMPLE 14

[0079] In this example, an interlayer film was prepared as follows. At first, 10 g of a methylethyl ketone solution containing 20 wt% of the ATO ultra-fine particles dispersed in the solution, and 150 g of pure 3GH were added to 490 g of a polyvinyl butyral resin. Then, this mixture was kneaded, with the addition of the bond adjusting agent, the ultraviolet ray absorbing agent and the like, by a mixer equipped with three rollers, at about 80 °C under a pressure of about 20 mm Hg for about 1 hr. Then, from this kneaded mixture, an interlayer film having a thickness of about 0.8 mm was prepared in the same manner as in Example 1. Using the thus prepared interlayer film, a laminated glass was prepared in the

same manner as in Example 1.

[0080] The same evaluation tests as those of Example 1 were conducted on the laminated glass. The laminated glass was satisfactory with respect to each evaluation test. For example, T_v was 76.4%, T_s was 51.6%, and H was 0.4%.

EXAMPLE 15

[0081] In this example, an interlayer film was prepared as follows. At first, 490 g of a polyvinyl butyral resin was heated at about 100 °C such that this resin became a syrupy condition. Under this condition, 2 g of the ATO ultra-fine particles were added to this resin. Then, this mixture was kneaded, with the addition of the ultraviolet ray absorbing agent and the like, by a mixer equipped with three rollers, at about 80 °C for about 1 hr. Then, from this kneaded mixture, an interlayer film having a thickness of about 0.8 mm was prepared in the same manner as in Example 1. Using the thus prepared interlayer film, a laminated glass was prepared in the same manner as in Example 1.

[0082] The same evaluation tests as those of Example 1 were conducted on the laminated glass. The laminated glass was satisfactory with respect to each evaluation test. For example, T_v was 77.5%, T_s was 55.7%, and H was 0.2%.

[0083] It is needless to say that pummel values of the laminated glasses of Examples 1, 2 and 5-15 can be adjusted for use as an architectural or automotive laminated glass.

Claims

35 1. A laminated glass comprising:
 first and second transparent glass plates;
 an interlayer film interposed between said first
 and second glass plates and bonded to said
 glass plates, said interlayer film having a thick-
 ness of 0.2 to 1.2 mm, said interlayer film com-
 prising a polyvinyl butyral or an ethylene-vinyl-
 acetate copolymer; and
 40 ultra-fine particles which have a particle diam-
 eter of up to 0.2 μm and are dispersed in said
 interlayer film and are in an amount of 0.01 to
 10.0 wt %, based on the total weight of said interlayer film,
 to provide at least an insulation against heat caused by solar radiation, said ultra-fine particles comprising at least one mem-
 ber selected from the group consisting of

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 55 (1) ATO which is defined as being an anti-
 mony-doped tin oxide, SnO_2 doped with
 Sb, SnO_2 doped with Sb_2O_3 , a conductive
 antimony-containing tin oxide or a solid so-
 lution of tin oxide and antimony oxide,

(2) ITO which is defined as being a tin-doped indium oxide, a mixture of In_2O_3 and SnO_2 , an indium tin oxide, a conductive tin-containing indium oxide, In_2O_3 doped with Sn or a solid solution of indium oxide and tin oxide,
 5
 (3) a mixture of Co_2O_3 and Al_2O_3 ,
 (4) a mixture of TiO_2 , NiO , Co_2O_3 and ZnO , and
 (5) a mixture of Fe_2O_3 , ZnO and Cr_2O_3 .
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2. A laminated glass according to claim 1, wherein said ultra-fine particles comprise at least one member selected from the group consisting of
 15
 (1) ATO which is defined as being SnO_2 doped with Sb_2O_3 or a conductive antimony-containing tin oxide,
 (2) ITO which is defined as being a mixture of In_2O_3 and SnO_2 or a conductive tin-containing indium oxide,
 20
 (3) a mixture of Co_2O_3 and Al_2O_3 ,
 (4) a mixture of TiO_2 , NiO , Co_2O_3 and ZnO , and
 (5) a mixture of Fe_2O_3 , ZnO and Cr_2O_3 .
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3. A laminated glass according to Claim 1 or 2, wherein said ultra-fine particles have a particle diameter within a range from 0.001 to 0.15 μm .
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4. A laminated glass according to claim 1 or 2, wherein said interlayer film provides an ultraviolet rays insulation function.
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5. A laminated glass according to claim 1 or 2, wherein said ultra-fine particles are mixed with an organic resin.
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6. A laminated glass according to claim 1 or 2, wherein said interlayer film comprises at least one member selected from the group consisting of organic ultra-violet-ray-absorbing agents, organic heat-absorbing agents and pigments.
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7. Use of a laminated glass according to claim 1 or 2 as an architectural glass, wherein said ultra-fine particles are in an amount from 0.01 to 9 wt%, based on the total weight of said interlayer film.
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8. Use of a laminated glass according to claim 1 or 2 as an automotive window glass, wherein said ultra-fine particles are in an amount from 0.01 to 2.0 wt%, based on the total weight of said interlayer film.
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9. Use of a laminated glass according to claim 1 or 2 as a radio wave transmittable glass having a sheet resistivity within a range from 20 $\text{M}\Omega/\square$ to 10 $\text{G}\Omega/\square$
 10. A method of producing a laminated glass, comprising the steps of:
 15
 (a) interposing an interlayer film between first and second glass plates, said interlayer film comprising a polyvinyl butyral or an ethylene-vinylacetate copolymer,
 said interlayer film comprising ultra-fine particles which are dispersed therein and have a particle diameter of up to 0.2 μm , thereby providing at least an insulation against heat caused by solar radiation,
 said ultra-fine particles comprising at least one member selected from the group consisting of
 20
 (1) ATO which is defined as being an antimony-doped tin oxide, SnO_2 doped with Sb, SnO_2 doped with Sb_2O_3 , a conductive antimony-containing tin oxide or a solid solution of tin oxide and antimony oxide,
 (2) ITO which is defined as being a tin-doped indium oxide, a mixture of In_2O_3 and SnO_2 , an indium tin oxide, a conductive tin-containing indium oxide, In_2O_3 doped with Sn or a solid solution of indium oxide and tin oxide,
 (3) a mixture of Co_2O_3 and Al_2O_3 ,
 (4) a mixture of TiO_2 , NiO , Co_2O_3 and ZnO , and
 (5) a mixture of Fe_2O_3 , ZnO and Cr_2O_3 ;
 25
 (b) bonding together said first and second glass plates and said interlayer film.
 30
 11. A method according to claim 10, wherein said ultra-fine particles comprise at least one member selected from the group consisting of
 35
 (1) ATO which is defined as being SnO_2 doped with Sb_2O_3 or a conductive antimony-containing tin oxide,
 (2) ITO which is defined as being a mixture of In_2O_3 and SnO_2 or a conductive tin-containing indium oxide,
 (3) a mixture of Co_2O_3 and Al_2O_3 ,
 (4) a mixture of TiO_2 , NiO , Co_2O_3 and ZnO , and
 (5) a mixture of Fe_2O_3 , ZnO and Cr_2O_3 .
 40
 12. A method according to Claim 10 or 11, wherein said interlayer film is made of a raw material prepared by a method comprising the steps of:
 45
 (c) dispersing up to 80.0 wt% of said ultra-fine particles in a plasticizer solution, based on the total weight of said plasticizer solution and said ultra-fine particles, so as to prepare a first mixture;

(d) adding up to 50 wt% of said first mixture to a polyvinyl butyral or an ethylene-vinylacetate copolymer, based on the total weight of said polyvinyl butyral or said ethylene-vinylacetate copolymer, so as to prepare a second mixture;

(e) optionally adding at least one additive to said second mixture so as to prepare a third mixture; and

(f) kneading said third mixture to uniformly disperse therein said ultra-fine particles, thereby to prepare said raw material.

13. A method according to Claim 12, wherein, during the step (c), up to 20.0 wt% of said ultra-fine particles are dispersed in said plasticizer solution.

14. A method according to Claim 10 or 11, wherein said interlayer film is prepared by a method comprising the steps of:

- (c) uniformly dispersing said ultra-fine particles having a particle diameter within a range from 0.001 to 0.2 µm in, in a solvent which is capable of dissolving therein a polyvinyl butyral or an ethylene-vinylacetate copolymer, so that a first mixture is prepared;
- (d) adding said polyvinyl butyral or said ethylene-vinylacetate copolymer, an optional plasticizer and at least one other optional additive to said first mixture, so that a second mixture in which said polyvinyl butyral or said ethylene-vinylacetate copolymer is dissolved is prepared;
- (e) kneading said second mixture;
- (f) shaping said kneaded second mixture into a film; and
- (g) drying said film at a temperature from 50 to 110°C into said interlayer film.

15. A method according to Claim 10 or 11, wherein said interlayer film is made of a raw material which is prepared by a method comprising the steps of:

- (c) heating a polyvinyl butyral or an ethylene-vinylacetate copolymer at a temperature which is higher than a glass transition temperature thereof, said glass transition temperature being within a range from 55 to 90°C, so that said polyvinyl butyral or said ethylene-vinylacetate copolymer is softened; and
- (d) adding ultra-fine particles having a particle diameter from 0.001 to 0.2 µm to said softened polyvinyl butyral or said softened ethylene-vinylacetate copolymer, so that a first mixture is prepared; and
- (e) kneading said first mixture so as to uniformly disperse therein said ultra-fine particles, thereby preparing said raw material.

5 16. A method according to Claim 10 or 11, wherein said ultra-fine particles comprise a mixture of said at least one member and an organic resin to reduce bond strength between said interlayer film and said first and second glass plates.

10 17. A method according to Claim 16, wherein said ultra-fine particles comprise said at least one member coated with said organic resin.

15 18. A method according to Claim 10 or 11, wherein an embossing is formed on a surface of said interlayer film.

20 19. A method according to Claim 10 or 11, wherein a surface of said first and second glass plates is coated with a primer or an organic resin to reduce bond strength between said interlayer film and said first and second glass plates.

25 20. A method according to Claim 10 or 11, wherein the step (b) is conducted in an autoclave, or for a period of time from 20 to 40 minutes under a pressure of from about 0.98 to about 1.37 MPa, while an ambient temperature was raised from 110 to 140°C.

Patentansprüche

30 1. Verbundglasscheibe, umfassend:

erste und zweite transparente Glasscheiben; einen Zwischenschichtfilm, zwischengelegt zwischen diesen ersten und zweiten Glasscheiben und an diesen Glasscheiben verklebt, wobei dieser Zwischenschichtfilm eine Dicke von 0,2 bis 1,2 mm besitzt und dieser Zwischenschichtfilm ein Polyvinylbutyral- oder ein Ethylen-Vinylacetatcopolymeres umfaßt; und ultrafeine Teilchen, die einen Teilchendurchmesser von bis zu 0,2 µm haben und in diesem Zwischenschichtfilm dispergiert sind und in einer Menge von 0,01 bis 10,0 Gew.-%, bezogen auf das Gesamtgewicht dieses Zwischenschichtfilms, vorliegen, um wenigstens eine Isolierung gegen durch Sonnenstrahlung bewirkte Erwärmung zu liefern, wobei diese ultrafeinen Teilchen wenigstens ein Glied umfassen, das aus der Gruppe ausgewählt ist, die besteht aus:

- (1) ATO, das definiert ist als ein mit Antimon dotiertes Zinnoxid, SnO₂ dotiert mit Sb, SnO₂ dotiert mit Sb₂O₃, ein leitfähiges Antimon enthaltendes Zinnoxid oder eine feste Lösung von Zinnoxid und Antimonoxid,
- (2) ITO, das definiert ist als ein mit Zinn do-

tieretes Indiumoxid, eine Mischung von In_2O_3 und SnO_2 , ein Indiumzinnoxid, ein leitfähiges Zinn enthaltendes Indiumoxid, In_2O_3 dotiert mit Sn oder eine feste Lösung von Indiumoxid und Zinnoxid,
 (3) einer Mischung von Co_2O_3 und Al_2O_3 ,
 (4) einer Mischung von TiO_2 , NiO , Co_2O_3 und ZnO , und
 (5) einer Mischung von Fe_2O_3 , ZnO und Cr_2O_3 .

2. Verbundglasscheibe nach Anspruch 1, bei welcher diese ultrafeinen Teilchen wenigstens ein Glied umfassen, das aus der Gruppe ausgewählt ist, die besteht aus:
 (1) ATO, das definiert ist als SnO_2 dotiert mit Sb_2O_3 oder ein leitfähiges Antimon enthaltendes Zinnoxid,
 (2) ITO, das definiert ist als eine Mischung von In_2O_3 und SnO_2 oder ein leitfähiges Zinn enthaltendes Indiumoxid,
 (3) einer Mischung von Co_2O_3 und Al_2O_3 ,
 (4) einer Mischung von TiO_2 , NiO , Co_2O_3 und ZnO , und
 (5) einer Mischung von Fe_2O_3 , ZnO und Cr_2O_3 .

3. Verbundglasscheibe nach Anspruch 1 oder 2, bei welcher diese ultrafeinen Teilchen einen Teilchendurchmesser innerhalb eines Bereiches von 0,001 bis 0,15 μm haben.

4. Verbundglasscheibe nach Anspruch 1 oder 2, bei welcher dieser Zwischenschichtfilm eine Isolierungsfunktion für ultraviolette Strahlung liefert.

5. Verbundglasscheibe nach Anspruch 1 oder 2, bei welcher diese ultrafeinen Teilchen mit einem organischen Harz gemischt sind.

6. Verbundglasscheibe nach Anspruch 1 oder 2, bei welcher dieser Zwischenschichtfilm wenigstens ein Glied umfaßt, das aus der Gruppe ausgewählt ist, die aus organischen Ultraviolettsstrahlung absorbierenden Mitteln, organischen Wärme absorbierenden Mitteln und Pigmenten besteht.

7. Verwendung einer Verbundglasscheibe nach Anspruch 1 oder 2 als ein Bauglas, in welchem diese ultrafeinen Teilchen in einer Menge von 0,01 bis 9 Gew.-%, bezogen auf das Gesamtgewicht dieses Zwischenschichtfilms, vorliegen.

8. Verwendung einer Verbundglasscheibe nach Anspruch 1 oder 2 als ein Kraftfahrzeugscheiben Glas, in welchem diese ultrafeinen Teilchen in einer Menge von 0,01 bis 2,0 Gew.-%, bezogen auf das Gesamtgewicht dieses Zwischenschichtfilms, vorliegen.

9. Verwendung einer Verbundglasscheibe nach Anspruch 1 oder 2 als ein für Radiowellen durchlässiges Glas mit einem spezifischen Scheibenwiderstand innerhalb eines Bereiches von 20 $M\Omega$ bis 10 $G\Omega$.

10. Verfahren zur Herstellung einer Verbundglasscheibe, umfassend die Stufen von:
 (a) Zwischenlegen eines Zwischenschichtfilms zwischen erste und zweite Glasscheiben, wobei dieser Zwischenschichtfilm ein Polyvinylbutyral- oder ein Ethylen-Vinylacetatcopolymeres umfaßt,
 dieser Zwischenschichtfilm ultrafeine Teilchen umfaßt, die hierin dispergiert sind und einen Teilchendurchmesser von bis zu 0,2 μm haben, wodurch wenigstens eine Isolierung gegen durch Sonnenstrahlung bewirkte Wärme geliefert wird,
 wobei diese ultrafeinen Teilchen wenigstens ein Glied umfassen, das aus der Gruppe ausgewählt ist, die besteht aus:
 (1) ATO, das definiert ist als ein mit Antimon dotiertes Zinnoxid, SnO_2 dotiert mit Sb, SnO_2 dotiert mit Sb_2O_3 , ein leitfähiges Antimon enthaltendes Zinnoxid oder eine feste Lösung von Zinnoxid und Antimonoxid,
 (2) ITO, das definiert ist als ein mit Zinn dotiertes Indiumoxid, eine Mischung von In_2O_3 und SnO_2 , ein Indiumzinnoxid, ein leitfähiges Zinn enthaltendes Indiumoxid, In_2O_3 dotiert mit Sn oder eine feste Lösung von Indiumoxid und Zinnoxid,
 (3) einer Mischung von Co_2O_3 und Al_2O_3 ,
 (4) einer Mischung von TiO_2 , NiO , Co_2O_3 und ZnO , und
 (5) einer Mischung von Fe_2O_3 , ZnO und Cr_2O_3 und
 (b) Miteinanderverkleben dieser ersten und zweiten Glasscheiben und dieses Zwischenschichtfilms.

11. Verfahren nach Anspruch 10, bei welchem diese ultrafeinen Teilchen wenigstens ein Glied umfassen, das aus der Gruppe ausgewählt ist, die besteht aus:
 (1) ATO, das definiert ist als SnO_2 dotiert mit Sb_2O_3 oder ein leitfähiges Antimon enthaltendes Zinnoxid,
 (2) ITO, das definiert ist als eine Mischung von In_2O_3 und SnO_2 oder ein leitfähiges Zinn enthaltendes Indiumoxid,

(3) einer Mischung von Co_2O_3 und Al_2O_3 ,
 (4) einer Mischung von TiO_2 , NiO , Co_2O_3 und
 ZnO , und
 (5) einer Mischung von Fe_2O_3 , ZnO und Cr_2O_3 .

12. Verfahren nach Anspruch 10 oder 11, bei welchem dieser Zwischenschichtfilm aus einem Ausgangsmaterial gemacht ist, das nach einem Verfahren hergestellt ist, welches die Stufen umfaßt:

(c) Dispergieren bis zu 80 Gew.-% dieser ultrafeinen Teilchen in einer Weichmacherlösung, bezogen auf das Gesamtgewicht dieser Weichmacherlösung und dieser ultrafeinen Teilchen, zu Herstellung einer ersten Mischung;

(d) Zugabe von bis zu 50 Gew.-% dieser ersten Mischung zu einem Polyvinylbutyral- oder einem Ethylen-Vinylacetatcopolymeren, bezogen auf das Gesamtgewicht dieses Polyvinylbutyral- oder dieses Ethylen-Vinylacetatcopolymeren, zur Herstellung einer zweiten Mischung;

(e) wahlweise Zugabe wenigstens eines Zusatzstoffes zu dieser zweiten Mischung zur Herstellung einer dritten Mischung; und

(f) Kneten dieser dritten Mischung zum gleichmäßigen Dispergieren dieser ultrafeinen Teilchen hierin zur Herstellung dieses Ausgangsmaterials.

13. Verfahren nach Anspruch 12, bei welchem während der Stufe (c) bis zu 20,0 Gew.-% dieser ultrafeinen Teilchen in dieser Weichmacherlösung dispergiert werden.

14. Verfahren nach Anspruch 10 oder 11, bei welchem dieser Zwischenschichtfilm nach einem Verfahren hergestellt ist, welches die Stufen umfaßt:

(c) gleichmäßiges Dispergieren dieser ultrafeinen Teilchen, die einen Teilchendurchmesser innerhalb eines Bereiches von 0,001 bis 0,2 μm haben, in einem Lösungsmittel, das zur Auflösung eines Polyvinylbutyral- oder eines Ethylen-Vinylacetatcopolymeren hierin fähig ist, so daß eine erste Mischung hergestellt wird;

(d) Zugabe dieses Polyvinylbutyral- oder dieses Ethylen-Vinylacetatcopolymeren, eines wahlweisen Weichmachers und wenigstens eines anderen wahlweisen Zusatzstoffes zu dieser ersten Mischung, so daß eine zweite Mischung, in welcher dieses Polyvinylbutyral- oder dieses Ethylen-Vinylacetatcopolymeren aufgelöst ist, hergestellt wird;

(e) Kneten dieser zweiten Mischung;

(f) Formen dieser zweiten Mischung zu einem Film; und

(g) Trocknen dieses Films bei einer Temperatur von 50 bis 110 °C zu diesem Zwischenschichtfilm.

15. Verfahren nach Anspruch 10 oder 11, bei welchem dieser Zwischenschichtfilm aus einem Ausgangsmaterial gemacht ist, das nach einem Verfahren hergestellt ist, welches die Stufen umfaßt:

(c) Erhitzen eines Polyvinylbutyral- oder eines Ethylen-Vinylacetatcopolymeren auf eine Temperatur, die höher ist als ein Einfrierbereich hiervon, wobei dieser Einfrierbereich innerhalb eines Bereiches von 55 bis 99°C liegt, so daß dieses Polyvinylbutyral- oder dieses Ethylen-Vinylacetatcopolymeren erweicht wird; und

(d) Zugeben ultrafeiner Teilchen, die einen Teilchendurchmesser von 0,01 bis 0,2 μm haben, zu diesem erweichten Polyvinylbutyral- oder diesem erweichten Ethylen-Vinylacetatcopolymeren, so daß eine erste Mischung hergestellt wird; und

(e) Kneten dieser ersten Mischung, so daß die ultrafeinen Teilchen hierin gleichmäßig dispergiert werden, wodurch dieses Ausgangsmaterial hergestellt wird.

16. Verfahren nach Anspruch 10 oder 11, bei welchem diese ultrafeinen Teilchen eine Mischung von diesem wenigstens einen Glied und ein organisches Harz umfassen, um die Bindungsfestigkeit zwischen diesem Zwischenschichtfilm und diesen ersten und zweiten Glasscheiben zu reduzieren.

17. Verfahren nach Anspruch 16, bei welchem diese ultrafeinen Teilchen dieses wenigstens eine Glied, beschichtet mit diesem organischen Harz, umfassen.

18. Verfahren nach Anspruch 10 oder 11, bei welchem eine Prägung auf einer Oberfläche dieses Zwischenschichtfilms geformt wird.

19. Verfahren nach Anspruch 10 oder 11, bei welchem eine Oberfläche dieser ersten und zweiten Glasscheiben mit einem Primer oder einem organischen Harz beschichtet wird, um die Bindungsfestigkeit zwischen diesem Zwischenschichtfilm und diesen ersten und zweiten Glasscheiben zu reduzieren.

20. Verfahren nach Anspruch 10 oder 11, bei welchem die Stufe (b) in einem Autoklaven oder für eine Zeitspanne von 20 bis 40 Minuten unter einem Druck von etwa 0,98 bis etwa 1,37 MPa, während eine Umgebungstemperatur von 110 auf 140°C erhöht wurde, durchgeführt wird.

Revendications**1. Verre feuilleté comprenant:**

des première et seconde plaques de verre transparent; un film intercouche interposé entre lesdites première et seconde plaques de verre et collé auxdites plaques de verre, ledit film intercouche ayant une épaisseur de 0,2 à 1,2 mm, ledit film intercouche comprenant un polyvinyl butyral ou un copolymère d'éthylène-acétate de vinyle; et des particules ultrafines qui ont un diamètre de particule jusqu'à 0,2 µm et sont dispersées dans ledit film intercouche et sont en une quantité de 0,01 à 10,0% en poids, en se basant sur le poids total dudit film intercouche, pour produire au moins un isolement contre la chaleur provoquée par le rayonnement solaire, lesdites particules ultrafines comprenant au moins un membre sélectionné dans le groupe consistant en:

- (1) ATO qui est défini comme étant un oxyde d'étain dopé d'antimoine, SnO_2 dopé de Sb, SnO_2 dopé de Sb_2O_3 , un oxyde d'étain contenant de l'antimoine conducteur ou une solution solide d'oxyde d'étain et d'oxyde d'antimoine,
- (2) ITO qui est défini comme étant un oxyde d'indium dopé d'étain, un mélange de In_2O_3 et SnO_2 , un oxyde d'indium étain, un oxyde d'indium contenant de l'étain conducteur, In_2O_3 dopé de Sn ou une solution solide d'oxyde d'indium et d'oxyde d'étain,
- (3) un mélange de Co_2O_3 et Al_2O_3 ,
- (4) un mélange de TiO_2 , NiO , Co_2O_3 et ZnO , et
- (5) un mélange de Fe_2O_3 , ZnO et Cr_2O_3 .

2. Verre feuilleté selon la revendication 1, où lesdites particules ultrafines comprennent au moins un membre sélectionné dans le groupe consistant en

- (1) ATO qui est défini comme étant SnO_2 dopé de Sb_2O_3 ou un oxyde d'étain contenant de l'antimoine conducteur,
- (2) ITO qui est défini comme étant un mélange de In_2O_3 et SnO_2 ou un oxyde d'indium contenant de l'étain conducteur,
- (3) un mélange de Co_2O_3 et Al_2O_3 ,
- (4) un mélange de TiO_2 , NiO , Co_2O_3 et ZnO , et
- (5) un mélange de Fe_2O_3 , ZnO et Cr_2O_3 .

3. Verre feuilleté selon la revendication 1 ou 2, où lesdites particules ultrafines ont un diamètre de particule dans une gamme de 0,001 à 0,15 µm.

4. Verre feuilleté selon la revendication 1 ou 2, où ledit film intercouche produit une fonction d'isolement des rayons ultraviolets.

5. Verre feuilleté selon la revendication 1 ou 2, où lesdites particules ultrafines sont mélangées avec une résine organique.

10 6. Verre feuilleté selon la revendication 1 ou 2, où ledit film intercouche comprend au moins un membre sélectionné dans le groupe consistant en agents organiques absorbant les ultraviolets, agents organiques absorbant la chaleur et pigments.

15 7. Utilisation d'un verre feuilleté selon la revendication 1 ou 2, en tant que verre pour l'architecture, où lesdites particules ultrafines sont en une quantité de 0,01 à 9% en poids, en se basant sur le poids total dudit film intercouche.

20 8. Utilisation d'un verre feuilleté selon la revendication 1 ou 2, en tant que verre de fenêtre d'automobile, où lesdites particules ultrafines sont en une quantité de 0,01 à 2,0% en poids en se basant sur le poids total dudit film intercouche.

25 9. Utilisation d'un verre feuilleté selon la revendication 1 ou 2, en tant que verre transmettant les ondes courtes ayant une résistivité de feuille dans une gamme de 20 MΩ □ à 10 GΩ □

30 10. Méthode de production d'un verre feuilleté comprenant les étapes de :

35 (a) interposer un film intercouche entre des première et seconde plaques de verre, ledit film intercouche comprenant un polyvinyl butyral ou un copolymère d'éthylène-acétate de vinyle. ledit film intercouche comprenant des particules ultrafines qui y sont dispersées et ont un diamètre de particule jusqu'à 0,2 µm, pour ainsi produire au moins un isolement contre la chaleur provoquée par le rayonnement solaire, lesdites particules ultrafines comprenant au moins un membre sélectionné dans le groupe consistant en

40 (1) ATO qui est défini comme étant un oxyde d'étain dopé d'antimoine, SnO_2 dopé de Sb, SnO_2 dopé de Sb_2O_3 , un oxyde d'étain contenant de l'antimoine conducteur ou une solution solide d'oxyde d'étain et d'oxyde d'antimoine,

45 (2) ITO qui est défini comme étant un oxyde d'indium dopé d'étain, un mélange de In_2O_3 et SnO_2 , un oxyde d'indium étain, un oxyde d'indium contenant de l'étain conducteur, In_2O_3 dopé de Sn ou une solution

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solidé d'oxyde d'indium et d'oxyde d'étain,
 (3) Un mélange de Co_2O_3 et Al_2O_3 ,
 (4) Un mélange de TiO_2 , NiO , Co_2O_3 et
 ZnO , et
 (5) Un mélange de Fe_2O_3 , ZnO et Cr_2O_3 ; et

(b) coller ensemble lesdites première et seconde plaques de verre et ledit film intercouche.

11. Méthode selon la revendication 10, où lesdites particules ultrafines comprennent au moins un membre sélectionné dans le groupe consistant en :

(1) ATO qui est défini comme étant SnO_2 dopé de Sb_2O_3 ou un oxyde d'étain contenant de l'antimoine conducteur,
 (2) ITO qui est défini comme étant un mélange de In_2O_3 et SnO_2 ou un oxyde d'indium contenant de l'étain conducteur.
 (3) Un mélange de Co_2O_3 et Al_2O_3 ,
 (4) un mélange de TiO_2 , NiO , Co_2O_3 et ZnO , et
 (5) un mélange de Fe_2O_3 , ZnO et Cr_2O_3 .

12. Méthode selon la revendication 10 ou 11, où ledit film intercouche est fait d'une matière première préparée par une méthode comprenant les étapes de :

(c) disperser jusqu'à 80,0% en poids desdites particules ultrafines, dans une solution d'un plastifiant, en se basant sur le poids total de ladite solution du plastifiant et desdites particules ultrafines, afin de préparer un premier mélange;
 (d) ajouter jusqu'à 50% en poids dudit premier mélange à un polyvinyl butyral ou un copolymère d'éthylène-acétate de vinyle, en se basant sur le poids total dudit polyvinyl butyral ou dudit copolymère d'éthylène-acétate de vinyle, afin de préparer un deuxième;
 (e) ajouter facultativement au moins un additif audit deuxième mélange afin de préparer un troisième mélange; et
 (f) malaxer ledit troisième mélange pour y disperser uniformément lesdites particules ultrafines pour ainsi préparer ladite matière première.

13. Méthode selon la revendication 12, où, pendant l'étape (c), jusqu'à 20,0% en poids desdites particules ultrafines sont dispersées dans ladite solution du plastifiant.

14. Méthode selon la revendication 10 ou 11, où ledit film intercouche est préparé par une méthode comprenant les étapes de :

(c) disperser uniformément lesdites particules ultrafines ayant un diamètre de particules dans une gamme de 0,001 à 0,2 μm dans un solvant

qui est capable d'y dissoudre un polyvinyl butyral ou un copolymère d'éthylène-acétate de vinyle de façon à préparer un premier mélange;
 (d) ajouter ledit polyvinyl butyral ou ledit copolymère d'éthylène-acétate de vinyle, un plastifiant facultatif et au moins un autre additif facultatif, audit premier mélange de façon qu'un deuxième mélange dans lequel est dissous ledit polyvinyl butyral ou ledit copolymère d'éthylène acétate de vinyle soit préparé; et
 (e) malaxer ledit deuxième mélange;
 (f) configurer ledit deuxième mélange malaxé en un film; et
 (g) sécher ledit film à une température de 50 à 110°C en ledit film intercouche.

15. Méthode selon la revendication 10 ou 11, où ledit film intercouche est fait d'une matière première qui est préparée par une méthode comprenant les étapes de :

(c) chauffer un polyvinyl butyral ou un copolymère d'éthylène acétate de vinyle à une température qui est plus haute qu'une température de transition vitreuse, ladite température de transition vitreuse étant dans une gamme de 55 à 90°C, de façon que ledit polyvinyl butyral ou ledit copolymère d'éthylène acétate de vinyle soit amollie; et
 (d) ajouter des particules ultra-fines ayant un diamètre de particule de 0,001 à 0,2 μm audit polyvinyl butyral amollie ou audit copolymère d'éthylène-acétate de vinyle amollie, de façon à préparer un premier mélange; et
 (e) malaxer ledit premier mélange afin d'y disperser uniformément lesdites particules ultrafines pour ainsi préparer ladite matière première.

16. Méthode selon la revendication 10 ou 11, où lesdites particules ultrafines comprennent un mélange dudit au moins un membre et d'une résine organique pour réduire la puissance de collage entre ledit film intercouche et lesdites première et seconde plaques de verre.

17. Méthode selon la revendication 16, où ledites particules ultrafines comprennent ledit au moins un membre enduit de ladite résine organique.

18. Méthode selon la revendication 10 ou 11, où un brossage est formé sur une surface dudit film intercouche.

19. Méthode selon la revendication 10 ou 11, où une surface desdites première et seconde plaques de verre est enduite d'une couche d'apprêt ou d'une résine organique pour réduire la force de collage

entre ledit film intercouche et lesdites première et seconde plaques de verre.

20. Méthode selon la revendication 10 ou 11, où l'étape (b) est entreprise dans un autoclave ou pendant une période de temps de 20 à 40 minutes sous une pression d'environ 0,98 à environ 1,37 MPa, tandis qu'une température ambiante était élevée de 110 à 140°C.

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